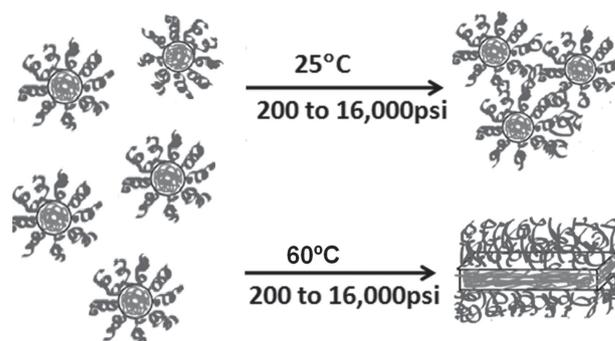


Polystyrene-*block*-Polyisoprene Diblock-Copolymer Micelles: Coupled Pressure and Temperature Effects

Gang Cheng,* Boualem Hammouda, Dvora Perahia*

The structural changes of diblock-copolymer micelles under pressures from 200 to 16 000 psi are investigated using small-angle neutron scattering (SANS). Asymmetric polystyrene-*block*-polyisoprene (PS-PI) diblock copolymers are dissolved in decane, a selective solvent for PI, to form spherical micelles with a core of PS and a corona of PI. The micellar solutions are put under pressure at temperatures of 25 to 60 °C. At room temperature, elevating the pressure from 200 to 16 000 psi has no effect on the size of the micelles. While the micellar solutions remain stable, instantaneous association of micelles is detected. In contrast to micelles at atmospheric pressure, increasing the temperature at elevated pressures does not lead to dissociation of micelles; instead, the micelles aggregate and evolve into sheet-like structures, reminiscent of a macroscopic phase separation. Furthermore, higher pressures lead to a smaller temperature range in which shape transitions take place.



1. Introduction

Block copolymers self-assemble into micelles when dissolved in a selective solvent, where the incompatibility between the blocks and the solvent drives their association. Structural studies of block-copolymer micelles as a

function of block length ratio, temperature, pH, and solvent selectivity reveal a variety of shapes, including spherical, disc-like, and cylindrical micelles as well as vesicles and bilayers.^[1] The wealth of nanostructures that can be prepared and the accurate control over the responses of each block to external stimuli has led to a number of applications from viscosity modifiers to drug delivery vehicles.^[2,3] One of the fascinating properties of block-copolymer micelles is their ability to change shape as the temperature or solvent compositions vary.^[4–8] For diblock-copolymer micelles with a “crew-cut” structure, where the thickness of the corona is smaller than the radius of the core, the variation in the micellar core–shell interfacial tension induces morphological transitions.^[4,6,7] A theoretical study has indicated that the excluded volume parameter of the soluble block and the volume fraction of the insoluble block in the core affect the transition as well.^[9]

In addition to the shape transition, the most commonly studied aspect of the temperature effect has been the association/dissociation of the block-copolymer micelles in solutions. The influence of temperature on the structure

Dr. G. Cheng
Beijing Key Laboratory of Bioprocess and College of Life
Science and Technology, Beijing University of
Chemical Technology
Beijing 100029, China
E-mail: gchengbuct@gmail.com
Dr. G. Cheng, Prof. D. Perahia
Materials Science and Engineering Program
and Department of Chemistry, Clemson University
South Carolina 29634, USA
E-mail: dperahi@g.clemson.edu
Dr. B. Hammouda
Center for Neutron Research, National Institute of
Standards and Technology
Gaithersburg, Maryland 20899, USA

of polystyrene-*block*-polyisoprene (PS-PI) micelles in decane has been studied at ambient pressure over a wide concentration range.^[10–12] With increasing temperature, the cores of the PS-PI micelles are swollen with solvents and the PS block becomes much more dynamic. This is followed by a breakdown of the micelles into smaller ones that eventually dissociate into single molecules. The inter-micellar interaction has been found to suppress the dissociation of micelles.^[12]

In comparison with the impact of temperature, the effects of pressure on micellization of block copolymers have been less explored, in part due to difficulties in sample environments.^[13] Previous studies utilize supercritical CO₂ (scCO₂),^[14,15] near-critical propane,^[16–19] near-critical trifluoromethane, and dimethyl ether, and so on^[20,21] to manipulate micellization of block copolymers. The solvent quality in these studies varies largely with pressure since they are highly compressible within the accessible experimental window. In the study of micellization of PS-PI in near-critical propane, decompression and cooling induce micelle formation while the micelles dissociate upon compression and heating.^[16] This has been explained by the phase behavior of the core-forming block, PS, which exhibits an upper critical solution temperature (UCST) in propane. It is also found that micellization pressure strongly depends on polymer concentration, molecular weight, and the block ratio.^[18] However, the impact of pressure on the shapes and sizes of PS-PI micelles in propane has not been investigated. More recently, a small-angle X-ray scattering (SAXS) investigation on 30% mass fraction PS-PI in diethylphthalate, a selective solvent for PS, demonstrates that the pressure swells the PS chains in the corona of the PS-PI micelles.^[22]

The pressure effects on aqueous micellar solutions can be further complicated by specific interactions such as hydrogen bonding.^[23,24] An investigation of poly(ethylene oxide)-*b*-poly(propylene oxide) (PEO-PPO) in aqueous solutions suggests that at low temperatures, increasing the pressure improves the solvent quality for the core-forming block, PPO.^[24] However, at higher temperatures, the pressure promotes the macroscopic phase separation (lamellar micelles aggregate and precipitate). The shell-forming block, PEO, exhibits a lower critical solution temperature (LCST) behavior in water, and it is proposed that the elevated pressure breaks the hydrogen bonding between PEO and water molecules at temperatures close to the LCST.

The present study investigates the structure of PS-PI micelles in subcritical decane by SANS with the aim of providing some insights into the effects of pressure on block-copolymer micelles in organic solvents. The structures of PS-PI micelles in a dilute solution are revealed by SANS, and the effect of pressure on the micellar dimension and shape transition is explored. The pressure is varied from atmospheric pressure up to 16 000 psi, and

the temperature is varied from 25 to 60 °C. The critical points for hydrogenated decane are as follows: $T_C = 344.65$ °C and $P_C = 305.35$ psi.^[25]

2. Experimental Section

2.1. Materials

PS-PI diblock copolymers were synthesized by anionic polymerization. The detailed information about the synthesis and the determination of molecular weight are given elsewhere.^[26] SANS studies were carried out on a diblock with a molecular weight of 27 800 g mol⁻¹ and a polydispersity index of 1.03, where the styrene block is 10 000 g mol⁻¹ and the isoprene block is 17 800 g mol⁻¹. Decane (D22) (Cambridge Isotope Laboratories, Inc.) was used as the solvent in the SANS experiments.

2.2. SANS

SANS measurements were performed in the Center for Neutron Research at the National Institute for Standards and Technology (NCSR) on NG3 SANS 30 m with a sample-to-detector distance of 910 cm and a neutron wavelength of $\lambda = 6$ Å ($\Delta\lambda/\lambda \approx 0.15$), spanning a q range of 0.00436–0.0491 Å⁻¹. Using the natural contrast between PS (the scattering length density of PS is 1.40×10^{-6} Å⁻²), PI (2.64×10^{-7} Å⁻²), and *d*-decane (6.60×10^{-6} Å⁻²), the total scattering function of the whole micelle, comprising both a core and a shell, was followed as a function of temperature and pressure. All scattering data were corrected for background, empty cell scattering, and sample transmission. Solvent scattering, normalized to its transmission and measured separately at each temperature, was then subtracted. All solutions exhibited isotropic distribution. 1D patterns were obtained through radially averaging the detector area. The scattering of the solvent was measured at each temperature at 1 atm; it was not measured at elevated pressures because of the small compressibility in this temperature range. For each temperature measurement and pressure setting, the solutions were annealed for at least 15 min prior to data collection. The pressure was generated using the NIST SANS in-situ hydraulic pressure cell composed of a stainless-steel frame and two sapphire windows to confine the sample. The pressure was varied between atmospheric pressure and 20 000 psi. The upper limit was dictated by the capability of the cell to retain the pressure with a highly volatile solvent, in a configuration appropriate for a solution.

SANS patterns were measured as a function of pressure at temperatures of 25, 35, 45, 55, and 60 °C for 1.1 wt% PS-PI in decane. At each temperature, the data were collected at 200, 4000, 8000, 12 000, and 16 000 psi.

3. Results and Discussion

SANS curves were measured as a function of pressure at temperatures of 25, 35, 45, 55, and 60 °C for 1.1% mass fraction of PS-PI in decane. At room temperature and

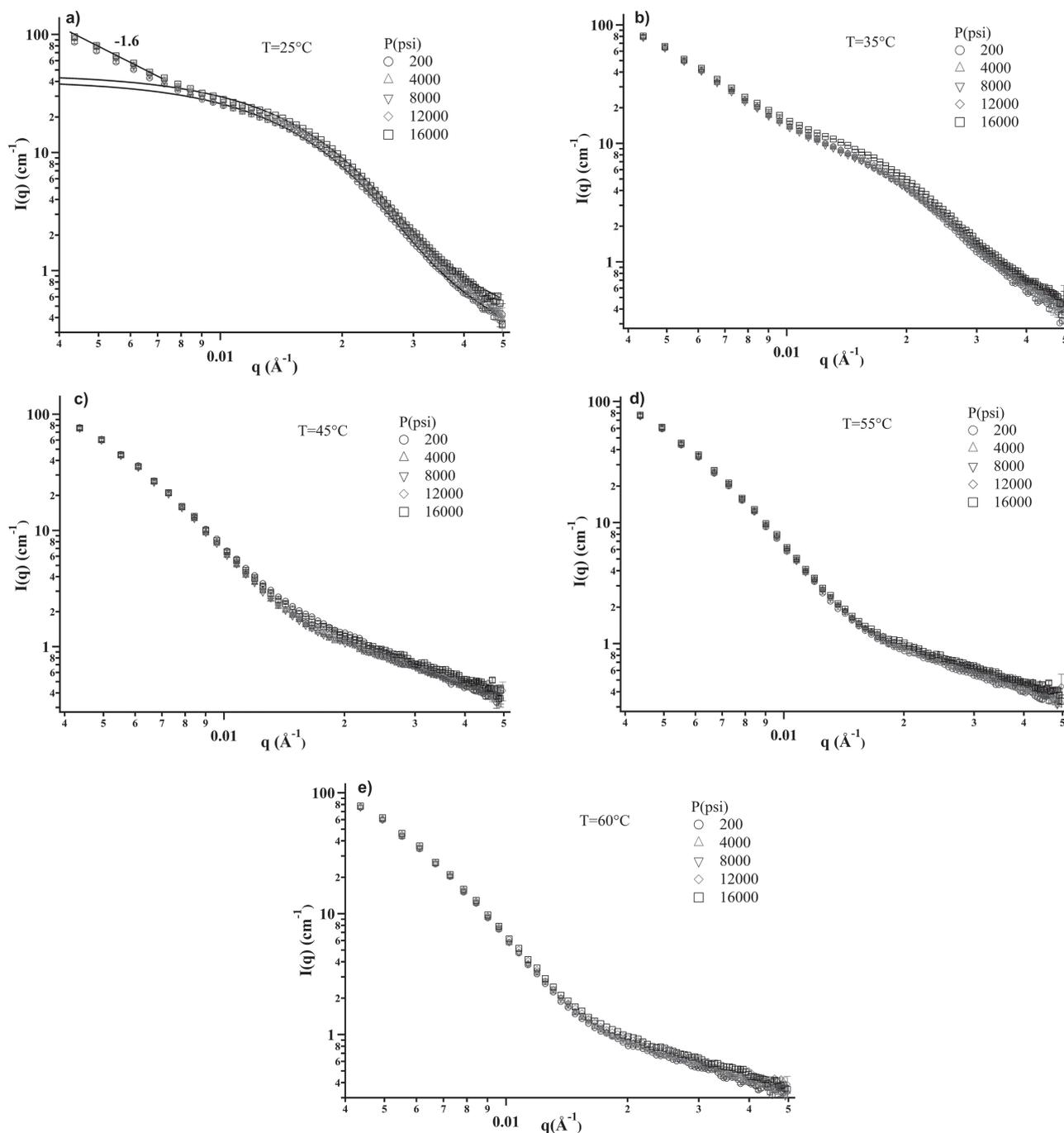


Figure 1. The pressure dependence of the SANS profiles of a 1.1 wt% PS-PI solution at: a) 25 °C, b) 35 °C, c) 45 °C, d) 55 °C, and e) 60 °C. The solid line in 1a corresponds to a fit to a core-Gaussian chain model. Error bars are smaller than the plotting symbols.

1 atm (14.7 psi), PS-PI diblock copolymers in decane form spherical micelles with the PS block in the core.^[12] SANS profiles at 200 psi of PS-PI in decane measured at 25 °C were shown in Figure 1a. Increasing the pressure to 200 psi resulted in an upturn at low q that exhibited a slope of -1.6 . Excluding the upturn at low q , the pattern at 200 psi was similar to that obtained for atmospheric pressure.^[12] The slope was retained as the pressure was increased to

16 000 psi, while there was a slight increase in the intensity in the middle q range due to the increased density of decane (Table 1).^[27] As shown in Table 1, the density of decane increased by 8% with pressure increasing from 200 to 16 000 psi. The upturn at low q may correspond to either the presence of loose instantaneous clusters formed by micelles^[28] or to the elongation of spherical micelles into oblates or cylinders.^[4] Fitting the SANS data to a model for

Table 1. Parameters obtained from fitting of the SANS data of 25 °C.

P [psi]	R_{core} [Å]	R_g [Å]	N_{agg}	Φ_{PS}	ρ_{decane} [g mL ⁻¹]
200	61 ± 2	47 ± 1	31	0.67 ± 0.10	0.846
4000	60 ± 3	48 ± 1	30	0.71 ± 0.10	0.868
8000	60 ± 3	47 ± 1	30	0.71 ± 0.10	0.886
12 000	60 ± 3	47 ± 1	30	0.71 ± 0.10	0.901
16 000	62 ± 3	46 ± 1	28	0.62 ± 0.10	0.914

micelles of oblate or cylindrical shape showed no improvement over that of spherical micelles. The low q upturn was therefore attributed to the formation of instantaneous micellar clusters, reflecting attractive interactions between the micelles.

The patterns, excluding the low q upturn, fit well to the core-Gaussian chain model (Figure 1a). The solid line on the data in Figure 1a corresponded to a form factor of micelles that consisted of a spherical core of PS and a corona that was described by a Gaussian chain model (core-Gaussian chain model).^[4,12] The scattering curves in the q range of the current work was dominated by the core-shell structure of block-copolymer micelles; and the scattering curves usually showed a q^{-2} behavior at larger q , characteristic of the Gaussian chain in the shell, which were not measured in this study. The fitting parameters included the core radius (R_{core}), the radius of gyration of polymer chains in the shell (R_g), and the aggregation number (N_{agg}). The polymer fraction in the core (Φ_{PS}) was calculated using the fitting results for the core radius, following Equation 1:

$$4/3\pi R_{\text{core}}^3 = N_{\text{agg}} V_{\text{PS}} / \Phi_{\text{PS}} \quad (1)$$

where V_{PS} is the dry volume of the PS block (15 950 Å³). The characteristics of the PS-PI micelles as a function of pressure, derived from fitting to the core-Gaussian chain model, were given in Table 1. As shown in Table 1, from 200 to 16 000 psi, the structure of the PS-PI micelles remained stable. The volume compressibility of the PS and PI block was reported to be -4.3% and -7.2% per kbar, respectively.^[29] Considering the effect of compressibility alone and assuming isotropic reduction in volume,^[29] the R_g of the PI block would have decreased by about 2.7% when the pressure was increased to 16 000 psi, which is about 1 Å. This was within the error bar of the SANS measurements.

The application of pressure usually reduces the compressibility difference between a polymer and a small molecule solvent, thus changing the polymer-solvent interactions.^[30] As a previous light scattering study of pressure effects on the micellization of poly(styrene-*block*-ethylene/propylene) in *n*-heptane showed, the solvent quality improved for PS as pressure reduced the compressibility difference between PS and heptanes.^[30]

More recently, SANS analysis of mixtures of scCO₂ and an LCST polymer blend of poly(styrene-*block*-acrylonitrile) and poly(methyl methacrylate) demonstrated that the addition of scCO₂ resulted in a decrease of the phase-separation temperature of the polymer blend. This change in the phase diagram was attributed to an increase in the Flory-Huggins interaction parameter between the polymers and scCO₂.^[31] We could not find any experimental data of pressure dependence of PS and PI homopolymers in decane.

One study of PS-PI diblock-copolymer melts using SAXS determined that raising pressure increased the segregation between the two blocks, and this led to an increase of the R_g of the block copolymer.^[29] It was noted that within the pressure range of 1450–10 150 psi, R_g increased linearly with pressure at a rate of 1 Å per kbar (1 kbar = 14 500 psi). Within the framework of a compressible random-phase approximation treatment of the diblock copolymers in the melt, an effective Flory-Huggins interaction parameter was constructed to describe the competition between the exchange energy density, which tends to increase with pressure, and the compressibility difference of the blocks, which often decreases with pressure.^[32] The increased segregation between PS and PI in the melt with pressure was reproduced by that theoretical treatment.^[32]

In a more recent SAXS study of the pressure dependences of PS-PI micelles in diethylphthalate, the thickness of the PS shell was found to increase about 10% with pressurization from 1500 to 7500 psi.^[22] This change was attributed mainly to the increased segregation between the two blocks with increasing pressure.^[22] In the current study, the structure of the PS-PI micelles remained stable upon pressurization. In addition to a better resolution provided by SAXS, it was noted that the polymer concentrations between these two studies were quite different. The current study probed ≈1% mass fraction of the polymer in solution where the micelles were rather isolated and did not interact, whereas prior work probed ≈30% mass fraction where the micelles were arranged in well-defined structures.^[22] We therefore eliminate some of the effects of the intermicellar interactions that contribute to the stability of the micelles as shown in

our previous studies.^[12] Pressure effects are concentration dependent. For example, for a 4.5% mass fraction poly(oxyethylene)-*b*-poly(oxybutylene) cubic gel, the unit cell and correlation length were found to be independent of pressure, while they varied significantly with pressure in a 9.5% mass fraction gel.^[13] Here, we probe dilute solutions where within the pressure changes applied to the system, the density of the solvent hardly changes; therefore, any structural change observed results from the compressibility of the polymer and changes in the incompatibility of the blocks that arise from the pressure. The unperturbed R_g of the PI blocks was calculated as $R_g = \sqrt{Nb^2/6} = 42 \text{ \AA}$, and the mean square end-to-end distance of the PS blocks was calculated as $R = \sqrt{Nb^2} = 67 \text{ \AA}$, where N is the number of Kuhn segments b , and $b = 8.2 \text{ \AA}$ for PI and 18 \AA for PS, respectively.^[33] As shown in Table 1, both the PS blocks in the core and PI blocks in the shell of the micelles were close to their unperturbed dimensions.

The pressure dependence (200–16 000 psi) of SANS profiles at 35, 45, 55, and 60 °C were shown in Figure 1b–e. At 35 °C, the scattering data retained some of the characteristics of spherical micelles. With the temperature fixed, applying pressure from 200 to 16 000 psi to the polymer solutions did not produce much changes in the SANS data, leaving it similar to that of 25 °C. This was also observed for the data of other temperatures. However, under a constant high pressure, raising temperature had a more dramatic effect on the micellar solution. The scattering intensity dropped dramatically in the intermediate q ranges and the pattern changed. The SANS data at these temperatures could not be fitted to known form factors, and therefore they were analyzed semi-quantitatively in the following discussion. Representative SANS patterns at 200 and 16 000 psi at different temperatures were shown in Figure 2. The slope at low q changed from -1.6 at 25 °C to -2.0 at 35 °C, as shown in Figure 2. The -2.0 slope corresponded to a sheet-like aggregate or a network.^[34] Considering the low concentration of the solution, a network was less likely. Thus, we asserted that a sheet-like aggregate developed at 35 °C. With further increasing temperature, these sheet-like aggregates grew in size, making the portion of the data that exhibits the -2.0 slope shift to even lower q (larger length scales).

Sheet-like aggregates are characterized by their transverse dimensions, which are often too large to be measured in a SANS experiment. Their thickness is obtained from the Guinier approximation for sheet-like aggregates:^[34]

$$I(q)q^2 \approx 2\pi\Phi t(\Delta\rho)^2 \exp(-q^2 t/12) \quad (2)$$

when:

$$t < 1/q < R_t$$

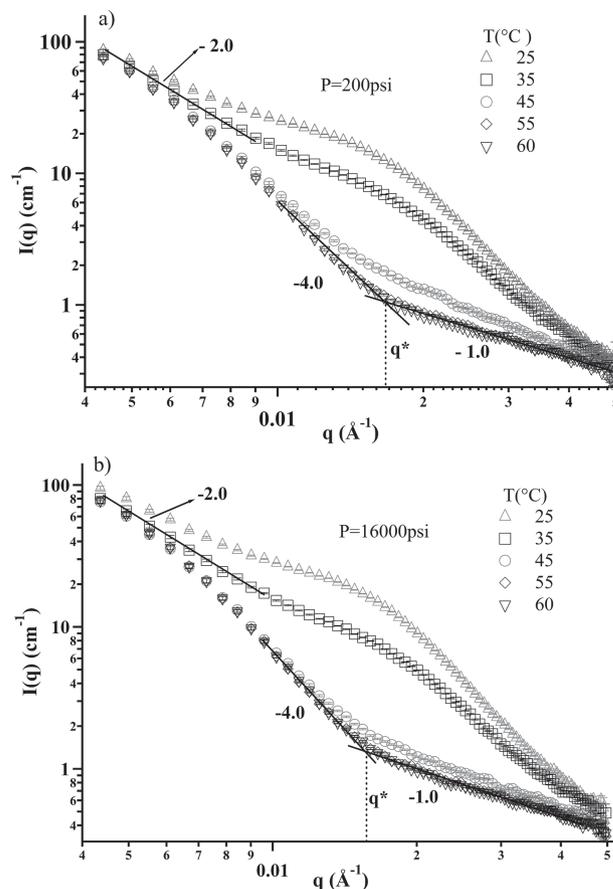


Figure 2. The temperature dependence of the SANS data of a 1.1% mass fraction PS-PI solution at a) 200 psi; b) 16 000 psi.

where $\Delta\rho$ is the difference in scattering length density between the sheet-like aggregate and the solvent, Φ is the volume fraction of the sheet-like aggregate, t is their thickness, and R_t is the smallest transverse dimensions. Figure 3 showed the Guinier plot of the SANS data collected at 200 psi. The solid lines corresponded to the fitting. The thickness of the sheet-like aggregate was extracted from their slope. Figure 4a introduced the temperature dependence of the thickness at various pressures. With increasing temperature, the thickness of the sheet-like aggregates increased from ≈ 150 to $\approx 350 \text{ \AA}$ before it leveled off, whereas the pressure hardly affected the thickness, as shown in Figure 4b.

At higher temperatures and pressures, a crossover from a slope of -4.0 to one of -1.0 was observed, as shown in Figure 2. This change in the slopes was consistent with a crossover from compact aggregates to the locally rod-like structure. The crossover q , defined here as q^* , occurred at 0.018 \AA^{-1} . This q value corresponds to a size of $2\pi/0.018$, which yields a value of 348 \AA . This value is close to the thickness of the sheet-like aggregates, 350 \AA , and also comparable to the diameter of one micelle (300 \AA , see Table 1) at 25 °C. To further

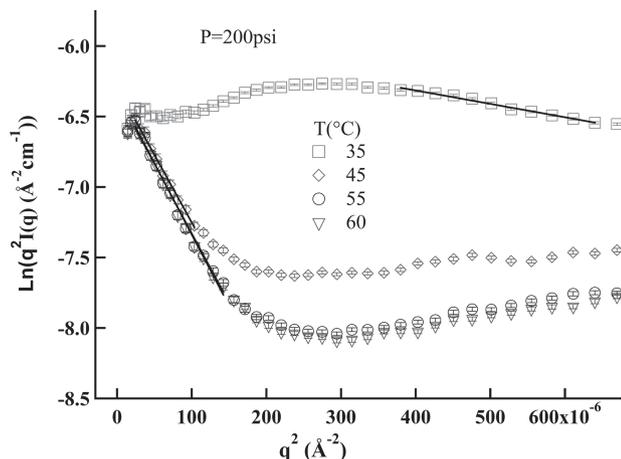


Figure 3. Guinier plots for sheet-like form factors at different temperatures for SANS data collected at 200 psi.

follow the variation of the scattering patterns with temperatures, the intensity at q^* was plotted as a function of pressure in Figure 5.

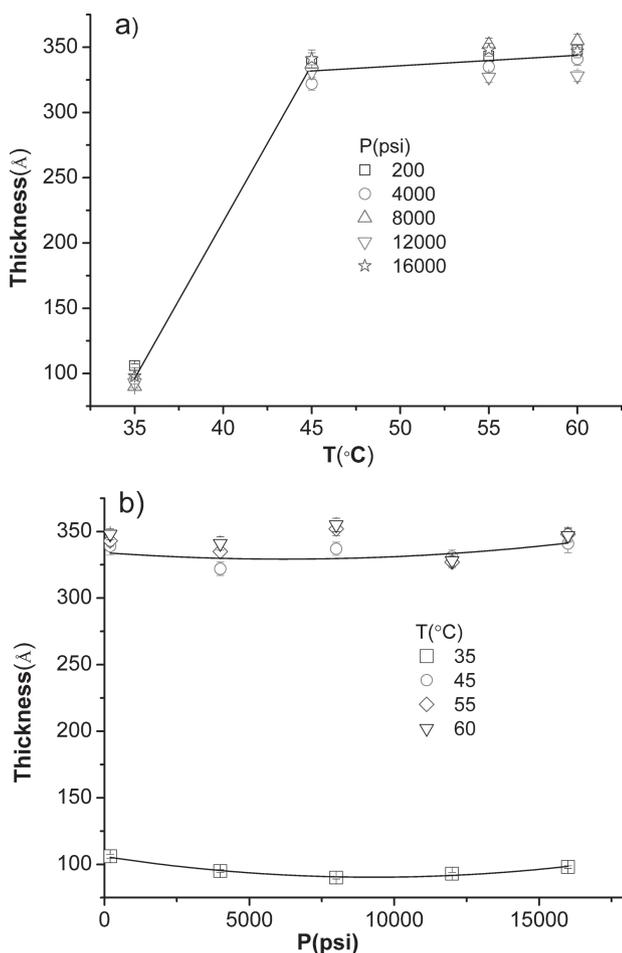


Figure 4. a) Variation of the thickness of the aggregates as a function of temperature at various pressures. b) Variation of the thickness of the aggregates as a function of pressure at various temperatures.

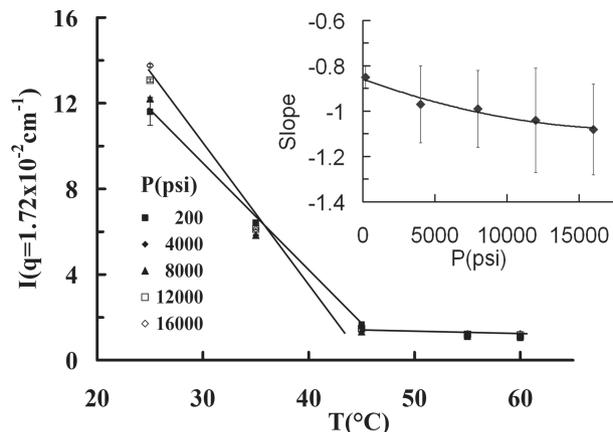


Figure 5. Variation of $I(q) = 0.018 \text{ \AA}^{-1}$ vs temperature at different pressures. The data points at 25, 35, and 45 °C were fitted to a straight line. For the sake of clarity, only two straight lines, corresponding to 200 and 16 000 psi, are shown. The changes in the slope of these lines are introduced in the inset. Fitting error bars correspond to one standard deviation.

With decreasing temperature, the intensity first sharply decreased and then leveled off. The decrease in intensity at q^* is a measure of the decrease in the fraction of spherical micelles in comparison with the sheet-like aggregates. The change of slope as function of pressure was shown as the inset of Figure 5. It suggested that the shape transition was accelerated with increased pressure.

Further insight into the conformation of the polymers within the sheet-like aggregates was obtained from q^* (0.018 \AA^{-1}). The crossover in q^* permits a measurement of the persistence length, L_p , of the scattering objects, using the equation: $L_p = 1.91 / q^*$.^[35] Within the studied pressure range, the L_p slightly varied from 121 to 129 Å. Therefore, these compact, sheet-like aggregates consisted of rod-like structures that exhibited a local stiffness on a length scale of $\approx 125 \text{ \AA}$. For a comparison, the mean square end-to-end distance of PS block was calculated as 67 Å, and of PI block was calculated as 103 Å. Therefore, the rod-like structure might correspond to the molecular sizes of PS-PI polymers in a compressed conformation.

The structural changes with increasing temperature at higher pressures suggest that the spherical PS-PI micelles undergo a macro phase separation via formation of micellar clusters and sheet-like aggregates, which is caused by the decreased solvent quality for PI blocks (i.e., the PI blocks exhibit an LCST in decane). It was reported that PI polymers in propane exhibit LCST behavior,^[16] therefore, it is our speculation that PI blocks in decane behaved similarly. At 1 atm, our prior work showed no signs of decreased solvent quality for PI block with increasing temperatures; thus, the thermodynamics of the PI blocks in decane may have changed upon pressurization. To the best of our knowledge, this has not been reported before. It is noted that the micellar shape transition occurs when the

micelles have a crew-cut structure.^[5] As shown in Table 1, the thickness of the shell is about 90 Å, which is roughly 1.5 times that of the core radius. It is believed that the PS–PI micelles resemble a structure that is not far away from the crew-cut one.

4. Conclusion

The influence of pressure on the structure of PS–PI micelles in decane at different temperatures was investigated using SANS. We showed that the low-concentration regime studies, the basic core–shell structure of PS–PI micelles at a constant temperature remained unperturbed. This rather surprising stability was attributed to the fact that over the pressure range exerted in this study, the solvent was hardly compressible. At room temperature, at these low concentrations, the pressure hardly affected the compatibility of the blocks and therefore no significant changes were observed in the structure of the micelle. In contrast, at elevated temperatures and pressures, the interaction of the polymers with the solvents was sufficiently large to result in faster shape changes and eventually a macro phase separation of the micelles.

Acknowledgements: The authors acknowledge the support of NSF DMR-0203660. G.C. acknowledges Beijing University of Chemical Technology. Certain commercial equipment, instruments, or materials are identified in this paper to foster understanding. Such identification does not imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the materials or equipment identified are necessarily the best available for the purpose. This work is based upon activities supported in part by the National Science Foundation under agreement no. DMR-0944772.

Received: December 5, 2013; Revised: February 15, 2014;
Published online: March 24, 2014; DOI: 10.1002/macp.201300760

Keywords: block-copolymer micelles; pressure; small-angle neutron scattering (SANS)

- [1] Y. Y. Mai, A. Eisenberg, *Chem. Soc. Rev.* **2012**, *41*, 5969.
- [2] E. van Ruymbeke, A. Parnvouxoglou, D. Vlassopoulos, G. Petekidis, G. Mountrichas, S. Pispas, *Soft Matter* **2010**, *6*, 881.
- [3] L. Y. Lin, N. S. Lee, J. H. Zhu, A. M. Nystrom, D. J. Pochan, R. B. Dorshow, K. L. Wooley, *J. Controlled Release* **2011**, *152*, 37.
- [4] J. Bang, S. Jain, Z. Li, T. P. Lodge, J. S. Pedersen, E. Kesselman, Y. Talmon, *Macromolecules* **2006**, *39*, 1199.
- [5] I. LaRue, M. Adam, E. B. Zhulina, M. Rubinstein, M. Pitsikalis, N. Hadjichristidis, D. A. Ivanov, R. I. Gearba, D. V. Anokhin, S. S. Sheiko, *Macromolecules* **2008**, *41*, 6555.
- [6] R. Lund, V. Pipich, L. Willner, A. Radulescu, J. Colmenero, D. Richter, *Soft Matter* **2011**, *7*, 1491.
- [7] G. V. Jensen, Q. Shi, G. R. Deen, K. Almdal, J. S. Pedersen, *Macromolecules* **2012**, *45*, 430.
- [8] E. Di Cola, C. Lefebvre, A. Deffieux, T. Narayanan, R. Borsali, *Soft Matter* **2009**, *5*, 1081.
- [9] E. B. Zhulina, M. Adam, I. LaRue, S. S. Sheiko, M. Rubinstein, *Macromolecules* **2005**, *38*, 5330.
- [10] J. Bang, K. Viswanathan, T. P. Lodge, M. J. Park, K. Char, *J. Chem. Phys.* **2004**, *121*, 11489.
- [11] M. J. Park, K. Char, J. Bang, T. P. Lodge, *Macromolecules* **2005**, *38*, 2449.
- [12] G. Cheng, B. Hammouda, D. Perahia, *Macromol. Chem. Phys.* **2014**, *215*, 341.
- [13] V. Castelletto, G. E. Newby, I. W. Hamley, L. Noirez, P. Baroni, *Langmuir* **2008**, *24*, 8319.
- [14] A. Triolo, F. Triolo, F. Lo Celso, D. E. Betts, J. B. McClain, J. M. DeSimone, G. D. Wignall, R. Triolo, *Phys. Rev. E* **2000**, *62*, 5839.
- [15] E. Yoshida, A. Mineyama, *Colloid Polym. Sci.* **2012**, *290*, 183.
- [16] W. Winoto, H. Adidharma, Y. Shen, M. Radosz, *Macromolecules* **2006**, *39*, 8140.
- [17] W. Winoto, S. P. Tan, Y. Q. Shen, M. Radosz, K. Hong, J. W. Mays, *Macromolecules* **2009**, *42*, 3823.
- [18] W. Winoto, S. P. Tan, Y. Q. Shen, M. Radosz, K. L. Hong, J. W. Mays, *Macromolecules* **2009**, *42*, 7155.
- [19] W. Winoto, M. Radosz, *Macromolecules* **2011**, *44*, 5392.
- [20] J. Green, Z. Tyrrell, M. Radosz, *J. Phys. Chem. C* **2010**, *114*, 16082.
- [21] Z. L. Tyrrell, Y. Q. Shen, M. Radosz, *J. Phys. Chem. C* **2011**, *115*, 11951.
- [22] Y. S. Liu, J. D. Spring, M. Steinhart, R. Bansil, *Macromolecules* **2012**, *45*, 9147.
- [23] N. Osaka, S. Miyazaki, S. Okabe, H. Endo, A. Sasai, K.-i. Seno, S. Aoshima, M. Shibayama, *J. Chem. Phys.* **2007**, *127*, 094905.
- [24] B. Clover, B. Hammouda, *Langmuir* **2010**, *26*, 6625.
- [25] D. Ambrose, J. Walton, *Pure Appl. Chem.* **1989**, *61*, 9.
- [26] C. C. Lin, S. V. Jonnalagadda, P. K. Kesani, H. J. Dai, N. P. Balsara, *Macromolecules* **1994**, *27*, 7769.
- [27] J. H. Dymond, R. Malhotra, *Int. J. Thermophys.* **1987**, *8*, 541.
- [28] V. Patel, J. Dey, R. Ganguly, S. Kumar, S. Nath, V. K. Aswal, P. Bahadur, *Soft Matter* **2013**, *9*, 7583.
- [29] D. A. Hajduk, P. Urayama, S. M. Gruner, S. Erramilli, R. A. Register, K. Brister, L. J. Fetters, *Macromolecules* **1995**, *28*, 7148.
- [30] D. A. Ylitalo, C. W. Frank, *Polymer* **1996**, *37*, 4969.
- [31] S. Inceoglu, N. P. Young, A. J. Jackson, S. R. Kline, S. Costeux, N. P. Balsara, *Macromolecules* **2013**, *46*, 6345.
- [32] J. Cho, *Macromolecules* **2002**, *35*, 5697.
- [33] M. Rubinstein, R. H. Colby, *Polymer Physics*, Oxford University Press, Oxford, UK; New York **2003**.
- [34] T. Zemb, P. Lindner, *Neutron, X-rays and Light. Scattering Methods Applied to Soft Condensed Matter*, Elsevier Science BV, North Holland, The Netherlands **2002**.
- [35] E. Buhler, F. Boué, *Macromolecules* **2004**, *37*, 1600.